



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 707 645 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(43) Date of publication:

04.10.2006 Bulletin 2006/40

(51) Int Cl.:

C22C 38/00 (2006.01)

C22C 38/12 (2006.01)

C22C 38/58 (2006.01)

C21D 9/46 (2006.01)

C23C 2/02 (2006.01)

C23C 2/06 (2006.01)

C23C 2/26 (2006.01)

(21) Application number: 05703854.9

(86) International application number:

PCT/JP2005/000624

(22) Date of filing: 13.01.2005

(87) International publication number:

WO 2005/068676 (28.07.2005 Gazette 2005/30)

(84) Designated Contracting States:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT L I LT LU MC NL PL PT RO SE SI SK TR

(30) Priority: 14.01.2004 JP 2004006999

14.01.2004 JP 2004007096

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**(54) HOT DIP ZINC PLATED HIGH STRENGTH STEEL SHEET EXCELLENT IN PLATING
ADHESIVENESS AND HOLE EXPANDING CHARACTERISTICS**

(57) The present invention provides hot dip galvanized high strength steel sheet excellent in plating adhesion and hole expandability and a method of production of the same, that is, hot dip galvanization steel sheet excellent in plating adhesion and hole expandability containing, by mass%, C: 0.08 to 0.35%, Si: 1.0% or less, Mn: 0.8 to 3.5%, P: 0.03% or less, S: 0.03% or less, Al: 0.25 to 1.8%, Mo: 0.05 to 0.35%, and N: 0.010% or less and having a balance of Fe and unavoidable impurities, said hot dip galvanized high strength steel characterized

in that the steel sheet has a metal structure having ferrite, bainite, by area percent, 0.5% to 10% of tempered martensite, and, by volume percent, 5% or more of residual austenite, and a method of production comprising annealing by a continuous annealing process at 680 to 930°C in temperature, then cooling to the martensite transformation point or less, then hot dip galvanizing the steel during which heating the steel to 250 to 600°C, then hot dip galvanizing it.

Description**TECHNICAL FIELD**

5 [0001] The present invention relates to a hot dip galvanized high strength steel sheet excellent in plating adhesion and hole expandability and a method of production of the same.

BACKGROUND ART

10 [0002] In recent years, improved fuel economy of automobiles and reduced weight of chasses have been increasingly demanded. To reduce the weight, the need for high strength steel sheet excellent in tensile strength and yield strength has been rising. However, along with the rise in strength, this high strength steel sheet has become difficult to shape. In particular, steel materials have fallen in elongation. As opposed to this, recently, TRIP steel (high residual austenite steel) high in both strength and elongation has come to be used for the frame members of automobiles.

15 [0003] However, conventional TRIP steel contains over 1% of Si, so there are the problems that the plating is difficult to uniformly adhere and the hot dip galvanization ability is poor. For this reason, hot dip galvanized high strength steel sheet reduced in the amount of Si and containing Al as an alternative has been proposed in Japan Patent No. 2962038 and Japanese Patent Publication (A) No. 2003-105486. However, the former continues to have a problem in the plating adhesion since the Si content is a relatively high amount of 0.53% or more. Further, the latter reduces the Si content to less than 0.2% to improve the plating adhesion, but residual austenite is built into it due to the relatively high cooling rate, so there was the problem that the cooling rate could not be stably controlled and therefore the quality of the material became unstable.

20 [0004] Further, there are also quite a few members which are worked by burring to expand the worked hole part and form a flange. Steel sheet also having a hole expandability as an important characteristic is therefore being demanded.

25 Conventional TRIP steel meeting this demand changes from residual austenite to martensite after induced plastic transformation and has a large hardness difference from ferrite, so there is the problem of an inferior hole expandability. Further, due to the demands from auto manufacturers and home electrical appliance manufacturers for making steel sheet rustproof, hot dip galvanized steel sheet has been spreading. In this way, various manufacturers have been changing over from conventional cold rolled steel sheet to surface treated steel sheet. Production setups have become necessary which shorten the production processes to enable large emergency and short delivery orders for surface treated steel sheet, in particular hot dip galvanized steel sheet, to be handled. However, in the case of high temperature annealed material or high strength steel sheet for producing the above-mentioned hot dip galvanization steel sheet, productivity is low due to the high temperature annealing. Therefore, in the case of large emergency orders/production of hot dip galvanized high strength steel sheet, there is the problem that production concentrates at the hot dip galvanization line having an annealing furnace before it and cannot be handled.

30 [0005] On the other hand, an ordinary continuous annealing line for annealing the sheet material of cold rolled steel sheet or electrogalvanized steel sheet generally has a high speed and high productivity. Regardless of this, there are problems that a change in production reduces the production load as explained above, sometimes there is no material being run, and the production line is idled. There was therefore the serious problem of an excess in production capacity.

DISCLOSURE OF THE INVENTION

40 [0006] The present invention has as its object to resolve the above-mentioned conventional problems and realize a hot dip galvanized high strength steel sheet excellent in plating adhesion and hole expandability and a method of production of the same on an industrial scale.

45 [0007] The inventors engaged in intensive studies on hot dip galvanized high strength steel sheet excellent in plating adhesion and hole expandability and a method of production of the same and as a result discovered that by optimizing the steel ingredients, that is, reducing the amount of Si and using Al as an alternative element, it is possible to improve the adhesion of hot dip galvanization, that by adding Mo to give the material superior properties of both strength and elongation, and that by cooling to the martensite transformation point or less before the hot dip galvanization process, then heating to the temperature required for plating, it is possible to industrially produce steel stable in quality and including residual austenite and tempered martensite and further to improve the hole expandability. That is, they discovered that by subjecting steel sheet of the ingredients designed based on the above discovery to recrystallization annealing in the continuous annealing process in the two ferrite/austenite phase range, then suitably overaging it in accordance with need, cooling to the martensite transformation point or less, then heating to the temperature required for plating for hot dip galvanization, a composite metal structure having ferrite as a main phase, having tempered martensite in an area percent of 0.5% to 10%, having a low temperature generated phase of residual austenite of a volume percent of 7% or more, and having a bainite phase is obtained and, in addition, the hole expandability is improved.

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Further, if performing the recrystallization annealing on the continuous annealing line and performing the hot dip galvanization on the continuous hot dip galvanization line, large emergency orders/production can also be handled. The present invention was made to solve the above problem and has as its gist the following.

- 5 (1) A hot dip galvanized high strength steel sheet excellent in plating adhesion and hole expandability containing C: 0.08 to 0.35%, Si: 1.0% or less, Mn: 0.8 to 3.5%, P: 0.03% or less, S: 0.03% or less, Al: 0.25 to 1.8%, Mo: 0.05 to 0.35%, and N: 0.010% or less and having a balance of Fe and unavoidable impurities, said hot dip galvanization steel sheet characterized in that said steel sheet has a metal structure having ferrite, bainite, by area ratio, 0.5% to 10% of tempered martensite, and, by volume percent, 5% or more of residual austenite.
- 10 (2) A method of production of a hot dip galvanized high strength steel sheet excellent in plating adhesion and hole expandability characterized by hot rolling a slab having the steel ingredients as set forth in (1), coiling the sheet at a temperature of 400 to 750°C, cooling, annealing by a continuous annealing process at a temperature of 680 to 930°C, cooling to the martensite transformation point or less, then hot dip galvanizing the sheet, during which heating to 250 to 600°C, then hot dip galvanizing it.
- 15 (3) A method of production of a hot dip galvanized high strength steel sheet excellent in plating adhesion and hole expandability as set forth in (2), characterized by cooling the steel sheet to the martensite transformation point or less of said continuous annealing process, then optionally pickling it, then pre-plating the steel sheet with one or more of Ni, Fe, Co, Sn, and Cu to 0.01 to 2.0 g/m² per side.
- 20 (4) A method of production of a hot dip galvanized high strength steel sheet excellent in plating adhesion and hole expandability as set forth in (2), characterized by alloying the galvanized layer aftersaid hot dip galvanization process.
- (5) A method of production of a hot dip galvanized high strength steel sheet excellent in plating adhesion and hole expandability as set forth in (2) or (4), characterized by post-treating said galvanized layer or galvannealed layer with one or more of chromate treatment, inorganic film coating, chemical conversion, and resin film coating.
- 25 (6) A hot dip galvanized high strength steel sheet excellent in plating adhesion and hole expandability characterized by comprising the hot dip galvanized high strength steel sheet of (1) further containing one or more selected from, by mass %, Ti: 0.01 to 0.3%, Nb: 0.01 to 0.3%, V: 0.01 to 0.3%, Cu: 1% or less, Ni: 1% or less, Cr: 1% or less, and B: 0.0001 to 0.0030%.
- 30 (7) A method of production of a hot dip galvanized high strength steel sheet excellent in plating adhesion and hole expandability as set forth in (2), characterized in that the hot dip galvanized high strength steel sheet of (1) further contains one or more selected from, by mass %, Ti: 0.01 to 0.3%, Nb: 0.01 to 0.3%, V: 0.01 to 0.3%, Cu: 1% or less, Ni: 1% or less, Cr: 1% or less, and B: 0.0001 to 0.0030%.

35 BEST MODE FOR WORKING THE INVENTION

[0008] First, the reasons for limitation of the ingredients and metal structure of the hot dip galvanized high strength steel sheet prescribed in the present invention will be explained.

[0009] 40 C is an essential ingredient from the viewpoint of securing strength or as a basic element for stabilizing the austenite, but the amount added has to be adjusted in relation to the amount of Si depending on the application. When the tensile strength required is a relatively low one of about 400 to 800 MPa and ductility or hot dip galvanizability is stressed, together with a low amount of Si (for example, 0.2% or less), the amount of C is made 0.08% to 0.3%, preferably 0.1 to 0.22%. On the other hand, when the tensile strength required is 600 MPa or more or further a high 900 MPa and simultaneously workability is to be given and hot dip galvanizability not obstructing working is to be provided, together with a high amount of Si (for example, 0.2 to 1.0%), the amount of C is made 0.12 to 0.35%, preferably 0.15 to 0.25%.

[0010] 45 Si is an effective element for securing strength, ductility, stabilizing austenite, and forming residual austenite. If the amount of addition is large, the hot dip galvanizability deteriorates, so less than 1.0% is added, but the amount of addition has to be adjusted depending on the application. When the tensile strength required is a relatively low 400 to 800 MPa or so and the ductility or hot dip galvanizability is stressed, Si is preferably added to less than 0.2%. When hot dip galvanizability is stressed, less than 0.1% is more preferable. When the tensile strength required is 600 MPa or more or further a high 900 MPa and simultaneously workability is to be given and hot dip galvanizability not obstructing work is to be provided, the amount of Si is made 0.2% to less than 1.0%. To secure hot dip galvanizability, the amount of Si is preferably 0.2% to less than 0.5%.

[0011] 50 Mn is an element which has to be added from the viewpoint of securing the strength and in addition delays the formation of carbides and is an element required for the formation of residual austenite. If Mn is less than 0.8%, the strength is not satisfactory. Further, the formation of residual austenite becomes insufficient and the ductility deteriorates. Further, if Mn is over 3.5%, the martensite increases instead of residual austenite and invites a rise in strength. Due to this, the variation in the final product becomes greater. In addition, the ductility is insufficient. Therefore, the steel cannot

be used as an industrial material. For this reason, the range of Mn was made 0.8 to 3.5%.

[0012] P is added in accordance with the level of strength required as an element raising the strength of the steel sheet, but if the amount of addition is large, it segregates at the grain boundary, so degrades the local ductility and simultaneously degrades the weldability, so the upper limit value of P was made 0.03%. Further, S is an element which forms MnS and degrades the local ductility and weldability. It is an element preferably not present in the steel, so the upper limit was made 0.03%.

[0013] Mo forms pearlite and reduces the residual austenite rate if less than 0.05%. Excessive Mo addition sometimes causes a drop in the ductility and deterioration of the chemical convertability, so 0.35% was made the upper limit. Preferably, the amount of addition of Mo is made 0.15% or less to obtain a high strength-ductility balance.

[0014] Al is an element required for causing residual austenite in the same way as Si. It is added to improve the plating adhesion in place of Si, promotes the formation of ferrite, and suppresses the formation of carbides so as to stabilize the austenite and simultaneously acts as a deoxidizing element. Stabilization of austenite requires addition of 0.25% or more of Al. On the other hand, even if Al is overly added, its effect becomes saturated and conversely the steel becomes embrittled. Simultaneously, the hot dip galvanizability is reduced. Therefore, the upper limit was made 1.8%.

[0015] N is an unavoidably included element, but when included in a large amount, not only is the aging effect deteriorated, but also the amount of deposition of AlN becomes greater and the effect of addition of Al is reduced, so 0.01% or less is preferably contained. Further, unnecessarily reducing the N increases the cost in the steelmaking process, so normally the amount of N is controlled to 0.0020% or more.

[0016] Further, in the present invention, in addition to the above ingredients, it is further possible to add one or more of Ti: 0.01 to 0.3%, Nb: 0.01 to 0.3%, V: 0.01 to 0.3%, Cu: 1% or less, Ni: 1% or less, Cr: 1% or less, and B: 0.0001 to 0.0030%. Ti, Nb, and V can be added for precipitation strengthening and for improvement of strength, but if 0.3% or more, the workability deteriorates. Further, the Cr, Ni, and Cu may also be added as strengthening elements, but if 1% or more, the ductility and chemical convertability deteriorate. Further, B may be added as an element for improving the local ductility and hole expandability, but if 0.0001% or less, the effect cannot be exhibited, while if 0.0030% or more, the elongation and plating adhesion deteriorate.

[0017] In the present invention, next, the metal structure explained with reference to the method of production is an extremely important requirement.

[0018] That is, the biggest feature in the metal structure of the hot dip galvanized high strength steel sheet according to the present invention is that the steel contains, by area percent, 0.5% to 10% of tempered martensite. This tempered martensite is obtained by taking the martensite formed in the cooling process after continuous annealing at 680 to 930°C and heating it to 250 to 600°C, preferably 460 to 530°C, for continuous hot dip galvanization and tempering. If the amount of the tempered martensite is less than 0.5%, no improvement of the hole expansion rate is seen, while if over 10%, the difference in hardness between structures becomes too large and the workability falls. Further, by securing, by volume percent, 5% or more, preferably 7% or more, of residual austenite, the tensile strength x ductility is strikingly improved. Further, when the tensile strength required is 600 MPa or more or further a high 900 MPa and simultaneously workability is to be given, the residual austenite is preferably 7% or more. Further, this tempered martensite, ferrite, bainite, and, by volume percent, 5% or more of residual austenite form the main phase. By including these in steel sheet in a good balance, it's believed the workability and hole expandability are improved.

[0019] Next, the method of production of hot dip galvanized high strength steel sheet according to the present invention will be explained. A slab having the above-mentioned steel ingredients is hot rolled under ordinary conditions, then the sheet is coiled at a temperature of 400 to 750°C. The reason the coiling temperature was made the above range of temperature was to change the structure after hot rolling to pearlite with a small lamellae distance or a mixed structure of pearlite and bainite, to facilitate melting of the cementite in the annealing process, to suppress scale formation, to improve the descaling ability, to increase the hard phase, and to keep the cold rolling from becoming difficult. Therefore, low temperature coiling in the temperature range of 400 to 750°C is preferable.

[0020] The thus coiled up hot rolled steel sheet is cold rolled under ordinary conditions to obtain cold rolled steel sheet. Next, this cold rolled steel sheet is recrystallization annealed in a coexistent two-phase temperature range of austenite and ferrite, that is, a temperature range of 680 to 930°C. If the annealing temperature is over 930°C, the structure in the steel sheet becomes a single austenite phase and the C in the austenite becomes sparse, so it is no longer possible to cause stable residual austenite to form in the later cooling. Therefore, the upper limit temperature was made 930°C. On the other hand, if less than 680°C, due to the insufficient solute C, the C of the austenite becomes insufficiently concentrated and the ratio of the residual austenite falls, so the lower limit temperature was made 680°C. The above annealed steel sheet is cooled to the martensite transformation point or less. The cooling means is not particularly limited and may be any of cooling by spraying water, cooling by evaporation, cooling by immersion in water, or cooling by gas jets. From the annealing to the cooling to the martensite transformation point or lower, overaging at a temperature of 300 to 500°C is preferable. This overaging is meant to efficiently transform the austenite to bainite to secure a bainite phase, further transform the martensite formed by the annealing to tempered martensite, and concentrate the C in the residual austenite for stabilization, so holding at a temperature range of 300 to 500°C for 60 seconds to 20 minutes is preferable.

[0021] Further, in the present invention, the steel is overaged, then cooled to the martensite transformation point or below to secure martensite. Note that the martensite transformation point Ms is found by $Ms(^{\circ}C) = 561 - 471 \times C(\%) - 33 \times Mn(\%) - 17 \times Ni(\%) - 17 \times Cr(\%) - 21 \times Mo(\%)$.

[0022] The reason why the hole expandability is improved is not clear, but it is believed by annealing and cooling to the martensite transformation point or less, then heating the steel at a low temperature for hot dip galvanization, the balance of hardness between the soft structure and hard structure is improved, the local elongation is improved, and thereby the hole expandability is improved.

[0023] Further, in the present invention, the steel sheet cooled to the martensite transformation point or less is pickled as required before pre-plating. By performing this pickling before pre-plating, the steel sheet surface can be activated and the plating adhesion of the pre-plating can be improved. Further, the oxides of Si, Mn, etc. formed on the steel sheet surface in the continuous annealing process can be removed to improve the adhesion in the later hot dip galvanization. This pickling is preferably performed in a pickling solution containing 2 to 20% of hydrochloric acid for 1 to 20 seconds. Note that this pickling may be followed by Ni flash plating. Further, when the cooling after recrystallization in the continuous annealing process is cooling by any of the means of cooling by spraying water, cooling by evaporation, or cooling by immersion in water, a pickling process is required at the outlet side of the continuous annealing process for removing the oxide film on the steel sheet surface formed during the continuous annealing or during the cooling, so a pickling facility is provided at the outlet side of the continuous annealing facility. Therefore, the oxides of Si, Mn, etc. formed on the steel sheet surface can be removed simultaneously with the removal of the oxide film on the steel sheet surface for greater efficiency. In this way, the pickling process may be efficiently performed by a facility attached to the continuous annealing process, but it may also be performed by a separately provided pickling line.

[0024] Further, in the present invention, to improve plating adhesion to the steel sheet cooled to the martensite transformation point or less, it is preferable to pre-plate it by one or more of Ni, Fe, Co, Sn, and Cu to 0.01 to 2.0 g/m² per side of the steel sheet, preferably 0.1 to 1.0 g/m². For the method of pre-plating, any of the methods of electroplating, dipping, and spray plating may be employed. If the amount of plating deposition is less than 0.01 g/m², the effect of improvement of adhesion by the pre-plating is not obtained, while if over 2.0 g/m², the cost rises, so the amount of plating was made 0.01 to 2.0 g/m² per side of the steel sheet.

[0025] The thus treated steel sheet is next hot dip galvanized, but the sheet is preferably pretreated before this hot dip galvanization process. This pretreatment means treatment to clean the surface of the steel sheet by a grinding brush etc. Note that this grinding brush preferably is a brush containing abrasive particles. A cleaning solution used is preferably warm water, a caustic soda solution, or both.

[0026] Further, to enable even large emergency orders/production to be handled, it is preferable that the existing continuous annealing process and hot dip galvanization process be separate lines, but the invention is not limited to this. In the case of separate lines, it is also possible to perform temper rolling or other shape correction to correct any loss of shape of the steel sheet in the continuous annealing furnace or divert the steel sheet to an electrolytic cleaning line to remove dirt etc. Further, it also becomes possible to predict the quality in advance since samples of the material can be obtained between the continuous annealing and hot dip galvanization.

[0027] The thus treated steel sheet is then galvanized by a hot dip galvanization process. In this hot dip galvanization process, the steel sheet is heated to a temperature at which the surface is activated or more, that is, a temperature range of 250 to 600°C. Note that if considering the difference in temperature between the galvanization bath and steel sheet, a temperature range of 460 to 530°C is preferred. The heating means is not limited, but radiant tubes or induction heating is preferred. To enable even large emergency orders/production to be handled, the heating furnace of an existing continuous hot dip galvanization line can be utilized. Further, steel sheet is already recrystallization annealed by the above-mentioned continuous annealing process, so there are the advantages that the sheet can be run at a higher speed than when directly transferred from the cold rolling process to the hot dip galvanization process and therefore the productivity is also improved. This is preferable when handling large emergency orders/production.

[0028] Further, the galvanized steel sheet obtained by galvanization at said hot dip galvanization process may further be alloyed at the plating layer to make the plating structure dense and obtain a hard, tough plating layer by heat treating it in a temperature range of 470 to 600°C to obtain hot dip galvannealed steel sheet. In particular, in the present invention, by alloying, it is possible to control the Fe concentration in the plating layer to for example 7 to 15 mass%.

[0029] Further, in the present invention, to improve the corrosion resistance and workability, the hot dip galvanized steel sheet or hot dip galvannealed steel sheet produced by the above process may be treated on its surface by one or more of chromate treatment, inorganic film coating, chemical conversion, or resin film coating.

Example 1

[0030] Steel slabs obtained by melting and casting steel having the compositions of ingredients shown in Table 1 in a vacuum melting furnace were reheated at 1200°C, then hot rolled at a temperature of 880°C and finally rolled to produce hot rolled steel sheets. These were then cooled, coiled at a coiling temperature of 600°C, and held at that

temperature for 1 hour for coiling heat treatment. The obtained hot rolled steel sheets were ground to remove the scale, cold rolled by a 70% reduction rate, then heated to a temperature of 770°C using a continuous annealing simulator, then held at that temperature for 74 seconds for continuous annealing. Next, the sheets were cooled by 10°C/s to 450°C and were processed by two methods of production, that is, the conventional method and the invention method, to produce galvanized steel sheets.

5 (1) Conventional method

[0031] After cooling to 450°C, the sheets were hot dip galvanized and further were hot dip galvannealed at a temperature of 500°C without pickling or pre-plating, were cooled to ordinary temperature, then were 1% temper rolled to obtain the final products. The mechanical properties, metal structures, hole expandabilities, plating adhesions, and other various characteristics of the products are shown in Table 2 (method of production i)).

10 (2) Method of present invention

[0032] After cooling to 450°C, the sheets were held at a temperature of 400°C for 180 seconds for overaging, then cooled to the martensite transformation point or less, pickled by 5% hydrochloric acid, pre-plated with Ni to 0.5 g/m² per side of the sheet, heated to a temperature of 500°C, hot dip galvanized and further hot dip galvannealed, cooled to ordinary temperature, then 1% temper rolled to obtain the final products. The mechanical properties, metal structures, hole expandabilities, plating adhesions, and other various characteristics of the products are shown in Table 3 (method of production ii)).

[0033] Note that the test and analysis methods of the tensile strength (TS), hole expansion rate, metal structure, residual austenite, tempered martensite, plating adhesion, and plating appearance shown in Table 2 and Table 3 were as follows:

- 25 · Tensile strength: Evaluated by L-direction tension of JIS No. 5 tensile test piece.
A TS of 540 MPa or more and a product of TSxEI (%) of 18,000 MPa or more was deemed passing.
- Hole expansion rate: Japan Iron and Steel Federation standard, JFS T1001-1996
The hole expansion test method was employed. A 10 mmΦ punched hole (die inside diameter of 10.3 mm, clearance of 12.5%) was expanded by a 60° vertex conical punch in the direction with the burr of the punched hole at the outside at a rate of 20 mm/min.

D: Hole diameter when crack passes through sheet thickness (mm)

Do: Initial hole diameter (mm)

35 A hole expansion rate of 50% or more was deemed passing.

- 40 · Metal structure: Observed under optical microscope, residual austenite rate measured by X-ray diffraction. Ferrite observed by Nital etching and martensite by repeller etching.
- Tempered martensite rate: Tempered martensite was quantized by polishing a sample by repeller etching (alumina finish), immersing it in a corrosive solution (mixed solution of pure water, sodium pyrophosphate, ethyl alcohol, and picric acid) for 10 seconds, then again polishing it, rinsing it, then drying the sample by cold air. The structure of the dried sample was observed under a magnification of 1000X and a 100 μm x 100 μm area was measured by a Luzex apparatus to determine the area% of the tempered martensite. Table 2 and Table 3 show the area percent of this tempered martensite as the "tempered martensite area%".
- Residual austenite rate: A test sheet was chemically polished to 1/4 thickness from its surface. The residual austenite was quantified from the integrated strength of the (200) and (210) planes of the ferrite by the MoKα-rays and the integrated strength of the (200), (220), and (311) planes of the austenite. A residual austenite rate of 5% or more was deemed "good". Table 2 and Table 3 show this residual austenite volume percent as the "residual γvol%".
- Plating adhesion: Evaluated from state of plating peeling of bent part in 60°V bending test.

50 Very good: Small plating peeling (peeling width less than 3 mm)

Good: Light peeling of extent not posing practical problem (peeling width of 3 mm to less than 7 mm)

Fair: Considerable amount of peeling observed (peeling width of 7 mm to less than 10 mm)

Poor: Extreme peeling (peeling width of 10 mm or more)

55 A plating adhesion of "very good" or "good" was deemed passing.

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Plating appearance: Visual observation

Very good: No nonplating or unevenness, even appearance

Good: No nonplating, uneven appearance of extent not posing practical problem

Fair: Remarkable uneven appearance

Poor: Nonplating and remarkable uneven appearance

A plating appearance of "very good" or "good" was deemed passing.

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Table 1

Steel type	C	Si	Mn	P	S	Al	Mo	N	Cu	Ni	Cr	Nb	Ti	V	B	Selective element		Class	
																Inv. range	Inv. range		
A	0.080	0.016	1.47	0.022	0.010	1.117	0.155	0.002	0.0001	0.0002	0.001	0.0220	0.0300	0.0002	0.0001	0.0001	0.0001	Inv. range	
B	0.088	0.191	1.42	0.003	0.010	1.329	0.099	0.002	0.0001	0.0002	0.0001	0.0002	0.0048	0.0002	0.0001	0.0001	0.0001	Inv. range	
C	0.098	0.069	2.80	0.007	0.010	0.552	0.140	0.003	0.0001	0.0002	0.0001	0.0280	0.0210	0.0002	0.0005	0.0005	0.0005	Inv. range	
D	0.109	0.052	1.29	0.030	0.002	0.540	0.235	0.004	0.2400	0.0001	0.0002	0.0002	0.0002	0.0002	0.0001	0.0001	0.0001	Inv. range	
E	0.133	0.026	2.56	0.002	0.010	0.852	0.050	0.003	0.0001	0.0002	0.4800	0.0002	0.0002	0.0002	0.0001	0.0001	0.0001	Inv. range	
F	0.135	0.187	0.80	0.004	0.013	0.854	0.168	0.004	0.0002	0.0001	0.0002	0.0440	0.0002	0.0002	0.0006	0.0006	0.0006	Inv. range	
G	0.136	0.072	1.91	0.001	0.012	1.504	0.111	0.002	0.0002	0.0001	0.0002	0.0410	0.0002	0.0002	0.0001	0.0001	0.0001	Inv. range	
H	0.195	0.029	2.44	0.026	0.023	1.017	0.300	0.005	0.0001	0.0002	0.0001	0.0340	0.0001	0.0220	0.0001	0.0001	0.0001	Inv. range	
I	0.184	0.128	1.38	0.027	0.019	0.840	0.102	0.002	0.0002	0.0001	0.0002	0.0250	0.0250	0.0230	0.0001	0.0001	0.0001	Inv. range	
J	0.190	0.100	2.32	0.017	0.009	0.302	0.061	0.002	0.0002	0.1920	0.0002	0.0002	0.0002	0.0002	0.0002	0.0001	0.0001	0.0001	Inv. range
K	0.229	0.067	1.54	0.006	0.001	0.300	0.198	0.002	0.0001	0.0002	0.0001	0.0420	0.0330	0.0002	0.0005	0.0005	0.0005	Inv. range	
L	0.245	0.051	0.98	0.007	0.014	1.656	0.064	0.003	0.0002	0.0001	0.0640	0.0002	0.0002	0.0002	0.0001	0.0001	0.0001	Inv. range	
M	0.261	0.140	1.58	0.002	0.002	0.388	0.066	0.010	0.0002	0.0001	0.0002	0.0780	0.0002	0.0002	0.0001	0.0001	0.0001	Inv. range	
N	0.288	0.169	1.59	0.004	0.011	0.912	0.123	0.002	0.0002	0.0001	0.0230	0.0250	0.0270	0.0005	0.0005	0.0005	0.0005	Inv. range	

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(continued)

Steel type	C	Si	Mn	P	S	Al	Mo	N	Cu	Ni	Cr	Nb	Ti	V	B	Class	Selective element	
																	Inv. range	Comp. ex.
O	0.291	0.013	1.76	0.017	0.023	1.024	0.125	0.003	0.0002	0.0001	0.0002	0.0002	0.00670	0.0001	0.0001	Inv. range		
P	0.300	0.158	1.98	0.022	0.015	0.850	0.098	0.002	0.0002	0.0001	0.0002	0.0270	0.0002	0.0220	0.0005			
Q	<u>0.078</u>	0.110	1.80	0.020	0.010	0.508	0.080	0.003	0.0001	0.0002	0.0002	0.0002	0.0002	0.0002	0.0001	Comp. ex.		
R	<u>0.324</u>	0.100	2.00	0.020	0.020	<u>0.070</u>	0.124	0.001	0.0002	0.0002	0.0001	0.0330	0.0290	0.0002	0.0005	Comp. ex.		
S	0.138	<u>0.320</u>	1.60	0.020	0.010	0.896	0.140	0.004	0.0001	0.0002	0.0001	<u>0.3300</u>	0.0002	0.0002	0.0001	Comp. ex.		
T	0.129	0.120	<u>0.40</u>	0.030	0.020	<u>0.767</u>	0.060	0.004	0.0002	0.0002	0.0002	<u>0.3600</u>	0.0002	0.0002	0.0001	Comp. ex.		
U	0.141	0.180	<u>3.20</u>	0.015	0.022	0.702	0.134	0.003	0.0002	0.0001	0.0002	0.0002	0.0002	0.0002	<u>0.0038</u>	Comp. ex.		
V	0.134	0.040	1.70	0.030	0.020	<u>0.185</u>	0.080	0.004	0.0002	0.0001	0.0002	0.0002	0.0002	<u>0.0410</u>	0.0001	Comp. ex.		
W	0.174	0.180	2.22	0.030	0.020	<u>1.903</u>	0.100	0.002	0.0001	0.0002	0.0001	0.0002	0.0002	0.0002	0.0001	Comp. ex.		
X	0.124	0.110	1.70	0.030	0.020	0.534	<u>0.025</u>	0.003	0.0002	0.0001	0.0002	0.0230	0.0280	0.0002	0.0005	Comp. ex.		
Y	0.155	0.140	2.02	0.030	0.020	<u>0.612</u>	<u>0.320</u>	0.004	0.0002	0.0001	0.0001	0.0260	0.0002	0.0240	0.0005	Comp. ex.		

Table 2/method of production i)

Experiment no.	Steel type	TS (MPa)	EL (%)	TSxEL TSxEL	Residual γ volume (%)	Tempered martensite area (%)	Hole expansion rate (%)	Plating adhesion	Plating appearance	class
1	A	562	34	19040	8.7	<u>≤0.1</u>	52	Very good	Very good	Comp. ex.
2	B	590	33	19437	7.9	<u>≤0.1</u>	50	<u>Fair</u>	Good	Comp. ex.
3	C	603	33	19833	9.5	<u>≤0.1</u>	50	Very good	Very good	Comp. ex.
4	D	666	30	19950	5.1	<u>≤0.1</u>	48	Very good	Very good	Comp. ex.
5	E	607	34	20570	9.2	<u>≤0.1</u>	52	Very good	Very good	Comp. ex.
6	F	633	34	21488	11.5	<u>≤0.1</u>	51	<u>Fair</u>	Good	Comp. ex.
7	G	621	35	21700	12.4	<u>≤0.1</u>	52	Very good	Very good	Comp. ex.
8	H	632	30	18900	5.1	<u>≤0.1</u>	50	<u>Fair</u>	Good	Comp. ex.
9	I	646	34	21930	12.4	<u>≤0.1</u>	50	Good	Very good	Comp. ex.
10	J	625	34	21182	9.8	<u>≤0.1</u>	50	<u>Fair</u>	Good	Comp. ex.
11	K	702	28	19628	9.9	<u>≤0.1</u>	47	Very good	Very good	Comp. ex.
12	L	686	29	19865	9.4	<u>≤0.1</u>	47	Very good	Very good	Comp. ex.
13	M	714	27	19224	5.2	<u>≤0.1</u>	47	Good	Very good	Comp. ex.
14	N	796	26	20670	12.5	<u>≤0.1</u>	45	Good	Very good	Comp. ex.
15	O	634	33	20856	13.2	<u>≤0.1</u>	50	Very good	Very good	Comp. ex.
16	P	816	26	21190	12.4	<u>≤0.1</u>	45	Good	Very good	Comp. ex.
17	Q	525	26	<u>13598</u>	<u>2.3</u>	<u>≤0.1</u>	45	Good	Very good	Comp. ex.
18	R	796	19	<u>15105</u>	8.5	<u>≤0.1</u>	30	<u>Fair</u>	Good	Comp. ex.
19	S	619	20	<u>12380</u>	6.4	<u>≤0.1</u>	48	<u>Poor</u>	<u>Poor</u>	Comp. ex.
20	T	515	26	<u>13364</u>	<u>2.2</u>	<u>≤0.1</u>	45	Good	Very good	Comp. ex.
21	U	770	19	<u>14592</u>	5.4	<u>≤0.1</u>	21	<u>Fair</u>	<u>Poor</u>	Comp. ex.
22	V	502	31	<u>15531</u>	<u>2.3</u>	<u>≤0.1</u>	51	Very good	Very good	Comp. ex.
23	W	614	28	<u>17192</u>	8.9	<u>≤0.1</u>	53	<u>Poor</u>	<u>Fair</u>	Comp. ex.

(continued)

Experiment no.	Steel type	TS (MPa)	EL (%)	TSxEL TSxEL	Residual γ volume (%)	Tempered martensite area (%)	Hole expansion rate (%)	Plating adhesion	Plating appearance	Class
24	X	<u>531</u>	35	18550	<u>1.5</u>	<u>≤0.1</u>	56	<u>Fair</u>	Good	Comp. ex.
25	Y	691	25	<u>17225</u>	<u>2.1</u>	<u>≤0.1</u>	<u>41</u>	<u>Fair</u>	<u>Fair</u>	Comp. ex.

Table 3/(method of production ii)

Experiment no.	Steel type	TS (MPa)	EL (%)	TSxEL	Residual γ volume (%)	Tempered martensite area (%)	Hole expansion rate (%)	Plating adhesion	Plating appearance	Class
1	A	545	37	20388	9.7	4.7	64	Very good	Very good	Inv. ex.
2	B	566	36	20186	8.5	4.3	60	Good	Very good	Inv. ex.
3	C	579	35	20249	10.4	7.5	61	Very good	Very good	Inv. ex.
4	D	646	33	21319	5.7	4.5	60	Very good	Very good	Inv. ex.
5	E	583	37	21397	9.9	6.2	63	Very good	Very good	Inv. ex.
6	F	608	36	21901	12.5	4.0	62	Good	Very good	Inv. ex.
7	G	602	39	23191	13.9	7.6	64	Very good	Very good	Inv. ex.
8	H	607	32	19658	5.5	9.1	60	Good	Very good	Inv. ex.
9	I	620	36	22351	13.5	6.4	60	Very good	Very good	Inv. ex.
10	J	606	37	22674	11.0	7.0	62	Good	Very good	Inv. ex.
11	K	674	30	20379	10.7	5.4	58	Very good	Very good	Inv. ex.
12	L	659	31	20244	10.2	3.5	58	Very good	Very good	Inv. ex.
13	M	693	30	20570	5.8	5.3	58	very good	Very good	Inv. ex.
14	N	764	28	21458	13.5	5.6	56	Very good	Very good	Inv. ex.
15	O	609	35	21290	14.4	6.3	60	Very good	Very good	Inv. ex.
16	P	792	29	22637	13.9	6.6	56	Very good	Very good	Inv. ex.
17	Q	504	28	14152	2.5	4.2	55	Very good	Very good	Comp. ex.
18	R	764	20	15390	9.3	10.5	38	Good	Very good	Comp. ex.
19	S	600	22	13209	7.2	5.0	60	Good	Good	Comp. ex.
20	T	494	28	13883	2.4	0.9	55	Very good	Very good	Comp. ex.
21	U	739	20	14887	5.9	10.3	27	Good	Good	Comp. ex.
22	V	487	34	16605	2.6	4.6	62	Very good	Very good	Comp. ex.
23	W	589	30	17825	9.6	6.8	65	Good	Good	Comp. ex.

(continued)

Experiment no.	Steel type	TS (MPa)	EL (%)	TSxEL	Residual γ volume (%)	Tempered martensite area (%)	Hole expansion rate (%)	Plating adhesion	Plating appearance	Class
24	X	<u>510</u>	37	18912	<u>1.6</u>	3.2	68	Good	Good	Comp. ex.
25	Y	670	27	<u>17762</u>	<u>2.4</u>	<u>10.2</u>	51	Good	Good	Comp. ex.

Example 2

[0034] Steel slabs obtained by melting and casting the steels of A, I, and P of the range of ingredients of the present invention described in Table 1 were reheated to 1200°C, then hot rolled at a temperature of 880°C for final rolling to obtain hot rolled steel sheets. The steel sheets were cooled at a cooling temperature of 600°C and held at that temperature for 1 hour for cooling heat treatment. The obtained hot rolled steel sheets were descaled by grinding and cold rolled by a reduction rate of 70%, then heated to a temperature of 770°C using a continuous annealing simulator and held at that temperature for 74 seconds for continuous annealing, cooled by 10°C/s to 450°C, then overaged by being held at a temperature of 400°C for 180 seconds, then cooled to the martensite transformation point or less. These steel sheets were subjected to the following five types of experiments:

Experiment 1 (invention example): pickling by 5% hydrochloric acid, Ni pre-plating to 0.5 g/m²

Experiment 2 (invention example): no pickling, Ni pre-plating to 0.5 g/m²

Experiment 3 (comparative example): pickling by 5% hydrochloric acid, Ni pre-plating to 0.005 g/m²

Experiment 4 (comparative example): pickling by 5% hydrochloric acid, no Ni pre-plating

Experiment 5 (invention example): no pickling, no Ni pre-plating

[0035] After this, the sheets were brush ground corresponding to surface cleaning at the inlet side of the continuous hot dip galvanization line, then heated to a temperature of 500°C for hot dip galvanization and further hot dip galvannealing, cooled to ordinary temperature, then 1% temper rolled to obtain the final products. The characteristics of the plating adhesions and plating appearances of the products are shown in Table 4.

Table 4/differences in pickling and pre-plating conditions

Experiment no.	Steel type	Plating adhesion	Plating appearance	Class
[1]	A	Very good	Very good	Inv. ex.
[2]	A	Very good	Good	Inv. ex.
[3]	A	Fair	Fair	Comp. ex.
[4]	A	Fair	Poor	Comp. ex.
[5]	A	Very good	Good	Inv. ex.
[1]	I	Very good	Very good	Inv. ex.
[2]	I	Very good	Good	Inv. ex.
[3]	I	Fair	Poor	Comp. ex.
[4]	I	Poor	Poor	Comp. ex.
[5]	I	Good	Good	Inv. ex.
[1]	P	Very good	Very good	Inv. ex.
[2]	P	Very good	Good	Inv. ex.
[3]	P	Fair	Poor	Comp. ex.
[4]	P	Poor	Poor	Comp. ex.
[5]	P	Good	Good	Inv. ex.

[0036] In Example 1, the invention examples of Table 3 are improved in hole expandability due to the increase in tempered martensite compared with the comparative examples of the same experiment numbers of Table 2. In addition, the pickling and pre-plating improve the plating adhesion and plating appearance. The comparative examples of Table 3 are improved in plating adhesion and plating appearance by the pickling and pre-plating, but the ingredients are outside the scope of the present invention, so the TS, TSxEI, and hole expansion rate do not reach the passing values.

[0037] In the differences of pickling and pre-plating conditions of Example 2, from Experiment 1, Experiment 2, and Experiment 5, pre-plating greatly improves the plating adhesion and plating appearance and, further, pickling is preferably performed before pre-plating. From Experiment 3, if the amount of pre-plating is small, there is no effect. From Experiment 4, with just pickling, the properties conversely deteriorate. The reason why with just pickling, conversely the plating adhesion and plating appearance deteriorate is that the surface is overly activated and is heated by the heating process

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of the continuous hot dip galvanization in that state, so oxides of Si, Mn, etc. of the steel sheet are formed at the steel sheet surface and degrade the platability.

Example 3

[0038] Steel slabs obtained by melting and casting steel having the compositions of ingredients shown in Table 5 in a vacuum melting furnace were reheated at 1200°C, then hot rolled at a temperature of 880°C and finally rolled to produce hot rolled steel sheets. These were then cooled, coiled at a coiling temperature of 600°C, and held at that temperature for 1 hour for coiling heat treatment. The obtained hot rolled steel sheets were ground to remove the scale, cold rolled by a 70% reduction rate, then heated to a temperature of 770°C using a continuous annealing simulator, then held at that temperature for 74 seconds for continuous annealing. Next, the sheets were cooled by 10°C/s to 450°C and were processed by two methods of production, that is, the conventional method and the invention method, to produce galvanized steel sheets.

(1) Conventional method

[0039] After cooling to 450°C, the sheets were hot dip galvanized and further were hot dip galvannealed at a temperature of 500°C without pickling or pre-plating, were cooled to ordinary temperature, then were 1% temper rolled to obtain the final products. The mechanical properties, metal structures, hole expandabilities, plating adhesions, and other various characteristics of the products are shown in Table 6 (method of production i)).

(2) Method of present invention

[0040] After cooling to 450°C, the sheets were held at a temperature of 400°C for 180 seconds for overaging, then cooled to the martensite transformation point or less, pickled by 5% hydrochloric acid, pre-plated with Ni to 0.5 g/m² per side of the sheet, heated to a temperature of 500°C, hot dip galvanized and further hot dip galvannealed, cooled to ordinary temperature, then 1% temper rolled to obtain the final products. The mechanical properties, metal structures, hole expandabilities, plating adhesions, and other various characteristics of the products are shown in Table 7 (method of production ii)).

[0041] Note that the test and analysis methods of the tensile strength (TS), hole expansion rate, metal structure, residual austenite, tempered martensite, plating adhesion, and plating appearance shown in Table 6 and Table 7 were as follows:

- Tensile strength: Evaluated by L-direction tension of JIS No. 5 tensile test piece.

A TS of 540 MPa or more and a product of TSxEI (%) of 18,000 MPa or more was deemed passing.

- Hole expansion rate: Japan Iron and Steel Federation standard, JFS T1001-1996

The hole expansion test method was employed. A 10 mmΦ punched hole (die inside diameter of 10.3 mm, clearance of 12.5%) was expanded by a 60° vertex conical punch in the direction with the burr of the punched hole at the outside at a rate of 20 mm/min.

$$\text{Hole expansion rate: } \lambda (\%) = \frac{(D - D_0)}{D_0} \times 100$$

D: Hole diameter when crack passes through sheet thickness (mm)

D₀: Initial hole diameter (mm)

A hole expansion rate of 50% or more was deemed passing.

- Metal structure: Observed under optical microscope, residual austenite rate measured by X-ray diffraction. Ferrite observed by Nital etching and martensite by repeller etching.

- Tempered martensite rate: Tempered martensite was quantized by polishing a sample by repeller etching (alumina finish), immersing it in a corrosive solution (mixed solution of pure water, sodium pyrophosphate, ethyl alcohol, and picric acid) for 10 seconds, then again polishing it, rinsing it, then drying the sample by cold air. The structure of the dried sample was observed under a magnification of 1000X and a 100 μm × 100 μm area was measured by a Luzex apparatus to determine the area% of the tempered martensite. Table 6 and Table 7 show the area percent of this tempered martensite as the "tempered martensite area%".

- Residual austenite rate: A test sheet was chemically polished to 1/4 thickness from its surface. The residual

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austenite was quantified from the integrated strength of the (200) and (210) planes of the ferrite by the MoK α -rays and the integrated strength of the (200), (220), and (311) planes of the austenite. A residual austenite rate of 5% or more was deemed "good". Table 6 and Table 7 show this residual austenite volume percent as the "residual γ vol%".

· Plating adhesion: Evaluated from state of plating peeling of bent part in 60°V bending test.

5

Very good: Small plating peeling (peeling width less than 3 mm)

Good: Light peeling of extent not posing practical problem (peeling width of 3 mm to less than 7 mm)

Fair: Considerable amount of peeling observed (peeling width of 7 mm to less than 10 mm)

Poor: Extreme peeling (peeling width of 10 mm or more)

10

A plating adhesion of very good or good was deemed passing.

· Plating appearance: Visual observation

15

Very good: Even appearance with no nonplating or unevenness

Good: No nonplating and uneven appearance of an extent not posing practical problem

Fair: Remarkable uneven appearance

Poor: Nonplating and remarkable uneven appearance

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A plating appearance of "very good" or "good" was deemed passing.

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Table 5

Steel type A	C	Si	Mn	P	S	Al	Mo	N	Cu	Ni	Cr	Nb	Ti	V	B	Optional element		Class	
																Inv. range	Inv. range		
B	0.183	0.42	1.37	0.002	0.010	0.64	0.07	0.003	0.0000	0.0001	0.0000	0.0220	0.0250	0.0002	0.0001	0.0002	0.0005	Inv. range	
C	0.187	0.56	3.45	0.023	0.003	1.99	0.11	0.002	0.0002	0.0000	0.0002	0.0290	0.0002	0.0002	0.0001	0.0002	0.0005	Inv. range	
D	0.198	0.25	2.57	0.011	0.012	0.99	0.32	0.003	0.0360	0.0210	0.0003	0.0002	0.0310	0.0002	0.0002	0.0001	0.0001	0.0001	Inv. range
E	0.209	0.26	1.60	0.016	0.012	1.66	0.30	0.001	0.0002	0.0001	0.0003	0.0260	0.0380	0.0002	0.0002	0.0005	0.0005	Inv. range	
F	0.221	0.32	1.72	0.020	0.024	1.26	0.25	0.002	0.0003	0.0003	0.0004	0.0002	0.0300	0.0002	0.0001	0.0001	0.0001	0.0001	Inv. range
G	0.223	0.20	3.50	0.018	0.030	0.58	0.07	0.002	0.0002	0.0250	0.0002	0.0002	0.0250	0.0002	0.0002	0.0002	0.0001	0.0001	Inv. range
H	0.225	0.53	2.34	0.021	0.013	1.42	0.13	0.003	0.0003	0.0003	0.0002	0.0004	0.0270	0.0002	0.0330	0.0001	0.0001	0.0001	Inv. range
I	0.253	0.80	1.46	0.017	0.012	1.80	0.11	0.010	0.0001	0.0002	0.0001	0.0002	0.0250	0.0250	0.0210	0.0001	0.0001	0.0001	Inv. range
J	0.253	0.30	2.80	0.022	0.004	0.81	0.05	0.000	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0005	0.0005	Inv. range
K	0.296	0.49	3.15	0.019	0.019	0.77	0.19	0.003	0.0002	0.0001	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0001	Inv. range
L	0.299	0.29	1.20	0.025	0.000	1.30	0.28	0.00	0.0003	0.0004	0.0000	0.0220	0.0240	0.0110	0.0001	0.0001	0.0001	Inv. range	
M	0.309	0.45	1.32	0.022	0.026	0.90	0.35	0.003	0.0001	0.0003	0.0320	0.0002	0.0002	0.0002	0.0002	0.0001	0.0001	Inv. range	
N	0.324	0.23	2.87	0.014	0.004	1.39	0.10	0.00	0.0003	0.0000	0.0002	0.0240	0.0002	0.0002	0.0002	0.0001	0.0001	Inv. range	
O	0.336	0.44	2.19	0.006	0.001	0.76	0.30	0.00	0.0004	0.0000	0.0002	0.0260	0.0002	0.0190	0.0005	0.0005	0.0005	Inv. range	
P	0.350	0.70	2.88	0.022	0.022	0.25	0.29	0.00	0.0001	0.0001	0.0001	0.0002	0.0002	0.0002	0.0270	0.0005	0.0005	Inv. range	
Q	0.110	0.60	2.18	0.018	0.023	1.04	0.13	0.001	0.0001	0.0002	0.0002	0.0002	0.0410	0.0002	0.0002	0.0001	0.0001	Comp. ex.	
R	0.390	0.30	1.59	0.026	0.011	1.68	0.33	0.002	0.0000	0.0003	0.0002	0.0230	0.3800	0.0002	0.0002	0.0005	0.0005	Comp. ex.	
S	0.222	0.81	2.77	0.005	0.004	1.66	0.19	0.003	0.0003	0.0002	0.0002	0.0002	0.3500	0.0001	0.0001	0.0001	0.0001	Comp. ex.	
T	0.317	0.38	0.71	0.025	0.005	0.64	0.19	0.001	0.0001	0.0002	0.0002	0.0220	0.0260	0.0001	0.0001	0.0001	0.0001	Comp. ex.	
U	0.293	0.23	3.70	0.016	0.011	0.86	0.12	0.002	0.0002	0.0002	0.0002	0.3600	0.0220	0.0002	0.0002	0.0005	0.0005	Comp. ex.	
V	0.186	0.27	1.73	0.002	0.025	0.23	0.10	0.003	0.0001	0.0001	0.0003	0.0280	0.0002	0.0250	0.0001	0.0001	0.0001	Comp. ex.	
W	0.261	0.26	1.32	0.006	0.018	1.83	0.20	0.001	0.0001	0.0000	0.0003	0.0002	0.0002	0.0002	0.0002	0.0036	0.0036	Comp. ex.	
X	0.244	0.24	3.07	0.014	0.006	1.18	0.04	0.001	0.0002	0.0003	0.0000	0.0220	0.0290	0.0002	0.0001	0.0001	0.0001	Comp. ex.	

(continued)

Steel	C	Si	Mn	P	S	Al	Mo	N	Cu	Ni	Cr	Nb	Ti	V	B	Optional element	Class
Y	0.155	0.54	2.06	0.024	0.007	0.74	<u>0.37</u>	0.003	0.0001	0.0000	0.0004	0.0002	0.0002	0.0330	0.0005	Comp. ex.	

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Table 6/method of production i)

	Exp. no.	Steel type	TS (MPa)	EL (%)	TSxEL	Res. γ vol. (%)	Temp. mart. area (%)	Hole expansion rate (%)	Plating adhesion	Plating appear.	Class
5	1	A	601	35	21035	9.5	<u>≤0.1</u>	55	Fair	Fair	Comp. ex.
10	2	B	666	33	21978	7.5	<u>≤0.1</u>	52	Fair	Fair	Comp. ex.
15	3	C	768	30	23040	11.4	<u>≤0.1</u>	48	Fair	Poor	Comp. ex.
20	4	D	770	26	20020	7.2	<u>≤0.1</u>	45	Good	Good	Comp. ex.
25	5	E	813	27	21951	7.3	<u>≤0.1</u>	45	Good	Good	Comp. ex.
30	6	F	807	25	20175	7.9	<u>≤0.1</u>	43	Good	Good	Comp. ex.
35	7	G	795	26	20670	8.1	<u>≤0.1</u>	45	Fair	Fair	Comp. ex.
40	8	H	827	28	23156	13.5	<u>≤0.1</u>	46	Good	Fair	Comp. ex.
45	9	I	845	27	22815	12.7	<u>≤0.1</u>	46	Poor	Poor	Comp. ex.
50	10	J	874	22	19228	7.1	<u>≤0.1</u>	41	Good	Good	Comp. ex.
55	11	K	856	26	22256	10.0	<u>≤0.1</u>	45	Fair	Fair	Comp. ex.
	12	L	954	21	20034	7.2	<u>≤0.1</u>	41	Good	Good	Comp. ex.
	13	M	938	21	19698	7.1	<u>≤0.1</u>	41	Fair	Fair	Comp. ex.
	14	N	924	23	21252	10.2	<u>≤0.1</u>	41	Fair	Fair	Comp. ex.
	15	O	965	20	19300	8.2	<u>≤0.1</u>	41	Good	Good	Comp. ex.
	16	P	944	23	21712	11.5	<u>≤0.1</u>	42	Fair	Poor	Comp. ex.
	17	Q	585	30	<u>17550</u>	<u>3.2</u>	<u>≤0.1</u>	48	Fair	Poor	Comp. ex.
	18	R	984	18	<u>17712</u>	<u>6.8</u>	<u>≤0.1</u>	38	Fair	Fair	Comp. ex.
	19	S	1025 17		<u>17425</u>	8.2	<u>≤0.1</u>	38	Poor	Poor	Comp. ex.
	20	T	557	31	<u>17267</u>	<u>2.1</u>	<u>≤0.1</u>	47	Good	Fair	Comp. ex.
	21	U	875	20	<u>17500</u>	7.4	<u>≤0.1</u>	37	Fair	Fair	Comp. ex.

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(continued)

5	Exp. no.	Steel type	TS (MPa)	EL (%)	TSxEL	Res. γ vol. (%)	Temp. mарт. area (%)	Hole expansion rate (%)	Plating adhesion	Plating appear.	Class
22	V	662	25	<u>16550</u>	<u>1.2</u>	<u>≤0.1</u>	<u>44</u>	Good	Good	Comp. ex.	
23	W	826	21	<u>17346</u>	10.2	<u>≤0.1</u>	<u>39</u>	Fair	Poor	Comp. ex.	
24	X	722	23	<u>16606</u>	<u>1.2</u>	<u>≤0.1</u>	<u>40</u>	Good	Good	Comp. ex.	
25	Y	615	24	<u>14760</u>	<u>0.2</u>	<u>≤0.1</u>	<u>39</u>	Fair	Fair	Comp. ex.	

Table 7/method of production ii)

20	Ex. no.	Steel type	TS (MPa)	EL (%)	TSxEL	Res. γ vol. (%)	Temp. mарт. area (%)	Hole exp. rate (%)	Plating adhesion	Plating appearance	Class
25	1	A	586	38	22150	10.5	4.3	67	Very good	Very good	Inv. ex.
30	2	B	629	35	22015	8.1	9.5	63	Very good	Good	Inv. ex.
35	3	C	741	32	23345	12.2	8.8	60	Good	Good	Inv. ex.
40	4	D	751	28	21081	7.9	8.4	56	Very good	Very good	Inv. ex.
45	5	E	768	29	21988	7.9	5.8	55	Very good	Very good	Inv. ex.
50	6	F	779	26	20442	8.5	6.0	53	Very good	Very good	Inv. ex.
55	7	G	775	28	21766	8.9	9.1	55	Good	Good	Inv. ex.
	8	H	782	30	23195	14.6	7.3	56	Very good	Very good	Inv. ex.
	9	I	815	28	23117	13.6	5.0	57	Good	Good	Inv. ex.
	10	J	852	24	20247	7.8	8.5	50	Very good	Very good	Inv. ex.
	11	K	809	28	22294	10.8	9.7	55	Good	Good	Inv. ex.
	12	L	921	22	20299	7.7	5.9	50	Very good	Very good	Inv. ex.
	13	M	915	23	20742	7.8	6.4	51	Very good	Very good	Inv. ex.
	14	N	873	24	21288	11.0	9.4	51	Good	Good	Inv. ex.
	15	O	931	21	19556	8.8	8.2	50	Very good	Very good	Inv. ex.
	16	P	920	25	22863	12.7	9.6	52	Good	Good	Inv. ex.

(continued)

Ex. no.	Steel type	TS (MPa)	EL (%)	TSxEL	Res. γ vol. (%)	Temp. marten. area (%)	Hole exp. rate (%)	Plating adhesion	Plating appearance	Class
17	Q	553	32	<u>17580</u>	<u>3.5</u>	6.6	58	Very good	Very good	Comp. ex.
18	R	950	19	<u>17947</u>	7.3	<u>10.8</u>	<u>47</u>	Good	Good	Comp. ex.
19	S	999	18	18349	9.0	8.7	<u>48</u>	Good	Good	Comp. ex.
20	T	526	33	<u>17296</u>	<u>2.3</u>	4.0	58	Very good	Very good	Comp. ex.
21	U	844	21	<u>17732</u>	7.9	<u>11.0</u>	<u>46</u>	Good	Good	Comp. ex.
22	V	645	27	<u>17427</u>	<u>1.3</u>	5.5	54	Very good	Very good	Comp. ex.
23	W	781	22	<u>17375</u>	11.0	4.9	<u>48</u>	Good	Good	Comp. ex.
24	X	697	24	<u>16826</u>	<u>1.3</u>	<u>10.2</u>	<u>50</u>	Good	Good	Comp. ex.
25	Y	600	26	<u>15542</u>	<u>0.2</u>	7.0	<u>49</u>	Good	Good	Comp. ex.

Example 4

[0042] Steel slabs obtained by melting and casting the steels of E, H, and P of the range of ingredients of the present invention described in Table 5 were reheated to 1200°C, then hot rolled at a temperature of 880°C for final rolling to obtain hot rolled steel sheets. The steel sheets were coiled at a coiling temperature of 600°C and held at that temperature for 1 hour for coiling heat treatment. The obtained hot rolled steel sheets were descaled by grinding and cold rolled by a reduction rate of 70%, then heated to a temperature of 770°C using a continuous annealing simulator and held at that temperature for 74 seconds for continuous annealing, cooled by 10°C/s to 450°C, then overaged by being held at a temperature of 400°C for 180 seconds, then cooled to the martensite transformation point or less. These steel sheets were subjected to the following five types of experiments:

Experiment 1 (invention example): Pickling by 5% hydrochloric acid, Ni pre-plating to 0.5 g/m²

Experiment 2 (invention example): No pickling, Ni pre-plating to 0.5 g/m²

Experiment 3 (comparative example): Pickling by 5% hydrochloric acid, Ni pre-plating to 0.005 g/m²

Experiment 4 (comparative example): Pickling by 5% hydrochloric acid, no Ni pre-plating

Experiment 5 (invention example): No pickling, no Ni pre-plating

[0043] After this, the sheets were brush ground corresponding to surface cleaning at the inlet side of the continuous hot dip galvanization line, then heated to a temperature of 500°C for hot dip galvanization and further hot dip galvannealing, cooled to ordinary temperature, then 1% temper rolled to obtain the final products. The characteristics of the plating adhesions and plating appearances of the products are shown in Table 8.

Table 8/difference in pickling and pre-plating conditions

Experiment no.	Steel type	Plating adhesion	Plating appearance	Class
[1]	E	Very good	Very good	Inv. ex.
[2]	E	Very good	Good	Inv. ex.
[3]	E	Fair	Poor	Comp. ex.

(continued)

Experiment no.	Steel type	Plating adhesion	Plating appearance	Class
5	[4]	E	<u>Poor</u>	<u>Poor</u> Comp. ex.
	[5]	E	Good	Inv. ex.
	[1]	H	Very good	Very good Inv. ex.
	[2]	H	Very good	Good Inv. ex.
	[3]	H	<u>Poor</u>	<u>Poor</u> Comp. ex.
10	[4]	H	<u>Poor</u>	<u>Poor</u> Comp. ex.
	[5]	H	Good	Good Inv. ex.
	[1]	P	Good	Good Inv. ex.
	[2]	P	Good	Good Inv. ex.
	[3]	P	<u>Poor</u>	<u>Poor</u> Comp. ex.
15	[4]	P	<u>Poor</u>	<u>Poor</u> Comp. ex.
	[5]	P	Good	Good Inv. ex.
	[1]	P	Good	Good Inv. ex.
	[2]	P	Good	Good Inv. ex.
	[3]	P	<u>Poor</u>	<u>Poor</u> Comp. ex.
20	[4]	P	<u>Poor</u>	<u>Poor</u> Comp. ex.
	[5]	P	Good	Good Inv. ex.

[0044] In Example 3, the invention examples of Table 7 are improved in hole expandability due to the increase in tempered martensite compared with the comparative examples of the same experiment numbers of Table 6. In addition, the pickling and pre-plating improve the plating adhesion and plating appearance. The comparative examples of Table 3 are improved in plating adhesion and plating appearance by the pickling and pre-plating, but the ingredients are outside the scope of the present invention, so the TS, TSxEI, and hole expansion rate do not reach the passing values.

[0045] In the differences in pickling and pre-plating conditions of Example 4, from Experiment 1, Experiment 2, and Experiment 5, pre-plating greatly improves the plating adhesion and plating appearance and, further, pickling is preferably performed before pre-plating. From Experiment 3, if the amount of pre-plating is small, there is no effect. From Experiment 4, with just pickling, the properties conversely deteriorate. The reason why with just pickling, conversely the plating adhesion and plating appearance deteriorate is that the surface is overly activated and is heated by the heating process of the continuous hot dip galvanization in that state, so oxides of Si, Mn, etc. of the steel sheet are formed at the steel sheet surface and degrade the platability.

INDUSTRIAL APPLICABILITY

[0046] According to the present invention, it becomes possible to provide hot dip galvanized high strength steel sheet excellent in plating adhesion and hole expandability used in auto parts, household electric appliance parts, etc. and becomes possible to flexibly handle changes in product type, changes in production due to increase production at various manufacturers, and large emergency short delivery orders/production.

Claims

1. A hot dip galvanized high strength steel sheet excellent in plating adhesion and hole expandability containing C: 0.08 to 0.35%, Si: 1.0% or less, Mn: 0.8 to 3.5%, P: 0.03% or less, S: 0.03% or less, Al: 0.25 to 1.8%, Mo: 0.05 to 0.35%, and N: 0.010% or less and having a balance of Fe and unavoidable impurities, said hot dip galvanization steel sheet characterized in that said steel sheet has a metal structure having ferrite, bainite, by area ratio, 0.5% to 10% of tempered martensite, and, by volume percent, 5% or more of residual austenite.
2. A method of production of a hot dip galvanized high strength steel sheet excellent in plating adhesion and hole expandability characterized by hot rolling a slab having the steel ingredients as set forth in claim 1, coiling the sheet at a temperature of 400 to 750°C, cooling, annealing by a continuous annealing process at a temperature of 680 to 930°C, cooling to the martensite transformation point or less, then hot dip galvanizing the sheet, during which heating to 250 to 600°C, then hot dip galvanizing it.
3. A method of production of a hot dip galvanized high strength steel sheet excellent in plating adhesion and hole

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expandability as set forth in claim 2, **characterized by** cooling the steel sheet to the martensite transformation point or less of said continuous annealing process, then optionally pickling it, then pre-plating the steel sheet with one or more of Ni,Fe,Co,Sn, and Cu to 0.01 to 2.0 g/m² per side.

- 5 4. A method of production of a hot dip galvanized high strength steel sheet excellent in plating adhesion and hole expandability as set forth in claim 2, **characterized by** alloying the galvanized layer after said hot dip galvanization process.
- 10 5. A method of production of a hot dip galvanized high strength steel sheet excellent in plating adhesion and hole expandability as set forth in claim 2 or 4, **characterized by** post-treating said galvanized layer or galvannealed layer with one or more of chromate treatment, inorganic film coating, chemical conversion, and resin film coating.
- 15 6. A hot dip galvanized high strength steel sheet excellent in plating adhesion and hole expandability **characterized by** comprising the hot dip galvanized high strength steel sheet of claim 1 further containing one or more selected from, by mass%, Ti: 0.01 to 0.3%, Nb: 0.01 to 0.3%, V: 0.01 to 0.3%, Cu: 1% or less, Ni: 1% or less, Cr: 1% or less, and B: 0.0001 to 0.0030%.
- 20 7. A method of production of a hot dip galvanized high strength steel sheet excellent in plating adhesion and hole expandability as set forth in claim 2, **characterized in that** the hot dip galvanized high strength steel sheet of claim 1 further contains one or more selected from, by mass%, Ti: 0.01 to 0.3%, Nb: 0.01 to 0.3%, V: 0.01 to 0.3%, Cu: 1% or less, Ni: 1% or less, Cr: 1% or less, and B: 0.0001 to 0.0030%.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2005/000624

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl⁷ C22C38/00, 38/12, 38/58, C21D9/46, C23C2/02, 2/06, 2/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl⁷ C22C38/00-38/60, C21D9/46-9/48, C23C2/00-2/40

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2005
Kokai Jitsuyo Shinan Koho	1971-2005	Toroku Jitsuyo Shinan Koho	1994-2005

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPI (DIALOG)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2003-13177 A (Kawasaki Steel Corp.), 15 January, 2003 (15.01.03), & EP 1254911 A2 & AU 200244435 A & CA 2387322 A1 & KR 2002093606 A & CN 1396295 A & US 2003/106622 A1	1-7
A	JP 2003-73773 A (Kobe Steel, Ltd.), 12 March, 2003 (12.03.03), & WO 02/061161 A1 & EP 1365037 A1 & US 2004/0074575 A1	1-7
A	JP 2003-239040 A (Nippon Steel Corp.), 27 August, 2003 (27.08.03), (Family: none)	1-7

 Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search 19 April, 2005 (19.04.05)	Date of mailing of the international search report 10 May, 2005 (10.05.05)
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INTERNATIONAL SEARCH REPORT		International application No. PCT/JP2005/000624
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2003-105491 A (Nippon Steel Corp.), 09 April, 2003 (09.04.03), (Family: none)	1-7

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2962038 B [0003]
- JP 2003105486 A [0003]